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COLLEGE OF ENGLAND

ON THE SYNTHESIS OF TRIBASIC ACIDS.

By Maxwell Simpson, M.D., F.R.S.

In a paper which appeared some time ago in the "Transactions of the Royal Society,"* I showed that the cyanides of the diatomic radicals (at least those which form glycols) when treated with potash, yield bibasic acids which contain respectively four equivalents of carbon more than the parent radicals. Analogy would lead us to infer that the cyanides of the triatomic radicals would suffer a corresponding decomposition when treated with the same reagent, and yield tribasic acids, containing respectively six equivalents of carbon more than the original radicals. Thus, as we obtain in this way from the cyanide of ethylene (to take a particular case) a bibasic acid of the composition $C_8H_6O_8$ (succinic acid), so from the tercyanide of allyl ($C_6H_5Cy_3$), if the analogy holds good, we ought to get a tribasic acid, having the composition $C_{12}H_8O_{12}$:—

$$C_4H_4Cy_2 + 2\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O_2\right) + 4HO = \left.\begin{matrix}C_8H_4O_4''\\K_2\end{matrix}\right\}O_4 + 2NH_3$$

$$C_6H_5Cy_3 + 3\left(\left.\begin{matrix}K\\H\end{matrix}\right\}O_2\right) + 6HO = \left.\begin{matrix}C_{12}H_5O_6'''\\K_3\end{matrix}\right\}O_6 + 3NH_3$$

The following experiments were performed with the view of testing the correctness of the above inference:—

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* Philosophical Transactions for 1861, p. 61.

The first step towards the solution of this problem is, of course, the preparation of the hitherto unknown body tercyanide of allyl. This body I succeeded in obtaining by exposing to the temperature of a water-bath for about 20 hours, a mixture of 1 equivalent of terbromide of allyl, 3 equivalents of pure cyanide of potassium, and a quantity of alcohol equal to three times the weight of the cyanide, contained in a large glass balloon with a reversed Liebig's condenser attached to it. At the expiration of this time I found that all the cyanide of potassium had been converted into bromide, and that the alcohol, which now contained impure tercyanide of allyl in solution, no longer gave a precipitate with water. The reaction which takes place is expressed by the following equation:—

$$C_6H_5Br_3 + 3KCy = C_6H_5Cy_3 + 3KBr.$$

As soon as the alcohol became cold, it was separated from the bromide of potassium by filtration, and distilled. The residue thus obtained was then digested with cold water and filtered, by which means it was disembarrassed of a large quantity of tarry matter, which remained on the filter.

Having in this way prepared the tercyanide of allyl, the next step is to submit it to the action of caustic potash. Accordingly the filtrate was treated with a strong solution of that alkali, and exposed to heat so long as ammonia continued to be evolved. The product, which now contained an organic acid combined with the potash, was evaporated considerably, and treated cautiously in a capacious basin, with nitric acid in excess. This liberates the organic acid, and at the same time partially destroys the impurities with which it is contaminated. The excess of nitric acid was then removed by evaporation, at as low a temperature as possible, and the dry residue treated with strong alcohol, which dissolved the organic acid, but not the nitre which accompanied it. The acid, obtained on filtering and distilling off the alcohol, was finally rendered quite pure by subjecting it, in a glass globe with a long neck, to the action of boiling undiluted nitric acid as long as red fumes continued to be evolved. The residue left after the evaporation of the nitric acid now crystallised readily from water. The crystals, dried at 100° Cent., gave numbers on analysis, which establish the formula $C_{12}H_8O_{12}$, as will be seen from the following table:—

		Theory.				
			per cent.	I.	II.	III.
C_{12}	..	72	40·91	40·63	41·24	41·34
H_8	..	8	4·54	4·66	4·82	4·47*
O_{12}	..	96	54·55	—	—	—
		176	100·00			

The reaction which generates this body, is explained by the equation given at the commencement of this paper. This acid forms colourless crystals, which are very soluble in water and alcohol, and sparingly soluble in ether. They have an agreeable acid taste. The free acid gives with acetate of lead an abundant precipitate, soluble in strong acetic acid. The neutralised acid forms with perchloride of iron a reddish brown precipitate, from which the acid can be partially removed by solution of ammonia. Neither chloride of barium nor chloride of calcium affects the neutralised acid. An abundant precipitate, however, makes its appearance on the addition of alcohol to the mixed solutions. It is a very stable body, not being decomposed by boiling concentrated nitric acid. These reactions resemble those of succinic acid. It is, however, readily distinguished from that acid by its behaviour on exposure to heat. Thus it melts, when exposed to the temperature of about 158° Cent., and when subjected to a higher temperature, suffers decomposition.

The following reaction is, perhaps, characteristic. The solution of the acid, when boiled with freshly precipitated oxide of mercury and filtered, yields on evaporation beautiful white crystals, which have a lustre equal to that of metallic silver.

The following is a description of the crystalline form of this acid, for which I am indebted to Professor Miller, of Cambridge :—†

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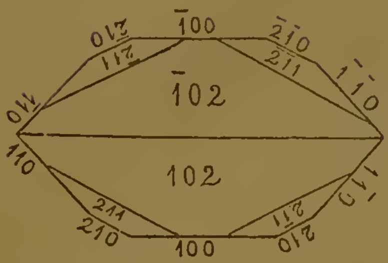
* The specimen of acid used in the last two analyses was prepared in a somewhat different manner. The divergence took place at the point in the above process where the mixture of free acid and nitre is digested with alcohol. The acid obtained on evaporating the alcohol, instead of being boiled with nitric acid, was converted into the silver-salt which was afterwards decomposed by sulphuretted hydrogen. It was twice crystallised from water before analysis.

† Professor Miller informs me that these numbers must be looked upon as rough approximations only, the crystals he operated upon not having been quite perfect.



PRISMATIC.

Simple forms: 100, 102, 110, 210, 211.

Angles between normals to the faces :—

100	102	....	66°	26′
102	$\bar{1}02$	....	47	8
100	110	....	46	0
110	$\bar{1}10$	....	88	0
100	210	....	27	22
100	211	....	37	41
110	211	....	32	23
210	211	....	26	59

Cleavage 100, very perfect and easily obtained.

This body has been named by Kekulé* carballylic acid. I cannot, however, accept this name without a slight modification of it, as recent researches have proved that it rightfully belongs to crotonic acid.† I propose, therefore, in order to avoid confusion, to call it *tri*-carballylic acid.

I regret to say I have not succeeded in obtaining the tercyanide of allyl in a fit state for analysis. On evaporating a portion of the alcohol, in the midst of which the terbromide of allyle and cyanide of potassium had reacted, a black mass was obtained, which I partially purified by solution in ether. On evaporating the ether, a brown liquid was left, which was very soluble in water. This, when gently heated with sodium, gave cyanide of sodium. When treated with potash, it yielded an organic acid and ammoniacal gas. With muriatic acid it gave an organic acid also, no doubt the same, and muriate of ammonia. These three reactions, coupled with the composition of the acid formed in the second, furnish almost conclusive evidence of the generation of tercyanide of allyle by the above process.

I have prepared and analysed several of the salts and ethers of tri-carballylic acid, of which I will now give an account.

Tri-carballylic Ether. $\left.\begin{matrix}C_{12}H_5O_6''' \\ (C_4H_5)_3\end{matrix}\right\}O_6$.—This body is readily prepared by conducting a stream of dry hydrochloric acid gas into a hot solution of the acid in absolute alcohol; as soon as the reaction is complete, the alcohol is distilled off and the residue washed with a solution of carbonate of soda, and then with pure water. On submitting the oil thus obtained to distillation, I found that almost the entire liquid passed over between 295° and 305° Cent. My analyses of this liquid establish the formula given above, as will be seen from the following table :—

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* Lehrbuch der Organischen Chemie. ii, 187. A preliminary notice of this acid has already appeared in the Proceedings of the Royal Society.

† Annalen der Chemie und Pharmacie. Band cxxxi, 58.

	Theory.		Experiment.	
		per cent.	I.	II.
C_{24} ..	144	55·38	54·59	54·86
H_{20} ..	20	7·69	7·83	7·43*
O_{12} ..	96	36·93		
	260	100·00		

This ether is a colourless liquid, slightly soluble in water, and having an acrid taste. It boils at about 300° Cent. Heated with solid potash, it suffers decomposition, alcohol being formed and the acid regenerated.

Tri-carballylic Amylic Ether. $\left.\begin{matrix} C_{12}H_5O_6''' \\ (C_{10}H_{11})_3 \end{matrix}\right\} O_6$.—Dry muriatic acid gas was conducted into a mixture of one part by weight of tri-carballylic acid and two parts of pure amylic alcohol, maintained at the temperature of boiling water. The acid gradually dissolved during the passage of the gas. As soon as it had entirely disappeared, the stream of gas was interrupted and the liquid was heated in a retort to 220° Cent. It was then partially purified by solution in absolute alcohol and in ether. The numbers I obtained on analysing this liquid, confirm the formula I have given, being as near the required numbers as could be expected from a liquid not purified by distillation.

	Theory.		Experiment.
		per cent.	
C_{42} ..	252	65·28	63·51
H_{38} ..	38	9·84	9·46
O_{12} ..	96	24·88	
	386	100·00	

This ether is a thick, oily liquid, heavier than water and having a very acrid taste. Its boiling point is beyond the range of the mercurial thermometer. I could not observe any symptoms of ebullition at 310° Cent. It bore this high temperature without suffering any apparent decomposition. On heating it in a retort with solid potash, a liquid distilled over, which I recognised to be amylic alcohol, by its boiling point and other properties. The acid of the ether remained in the retort united with the potash.

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* There was a slight loss of water in this analysis.

Glyceri-tricarballylate of Baryta. $\left.\begin{array}{c} C_{12}H_5O_6''' \\ C_6H_7O_4' \\ Ba_2 \end{array}\right\} O_6$.—A mixture of one part by weight of tricarballylic acid and two parts of pure glycerin was maintained in a sealed tube for several hours at the temperature of 200° Cent. The tube was then opened and a slight excess of a solution of caustic baryta added to its contents. The excess was afterwards precipitated by carbonic acid, and the filtered liquor evaporated to dryness on a water-bath. The residue was then treated with absolute alcohol to remove the uncombined glycerin, and finally dissolved in water and precipitated by alcohol. By these means a light buff-coloured precipitate was obtained, which would not crystallise. Its composition is, I have no doubt, truly expressed by the formula given above, although my analyses do not correspond very well with it.

The following are the numbers I obtained :—

		Theory.		Experiment.	
			per cent.	I.	II.
C_{18}	..	108·0	28·05	28·81	—
H_{12}	..	12·0	3·12	3·82	..
O_{16}	..	128·0	33·25	—	—
Ba_2	..	153·2	35·58	—	34·01

The acid in the above salt is bibasic; its composition is represented by the formula :—

$$\left.\begin{array}{c} C_{12}H_5O_6''' \\ C_6H_7O_4' \\ H_2 \end{array}\right\} O_6$$

Its formation is explained by the following equation :—

$$C_{12}H_8O_{12} + C_6H_8O_6 = C_{18}H_{14}O_{16} + 2HO.$$

Soda-salts of Tri-carballylic Acid.—The soda-salts of this acid are very soluble in water and difficult to crystallise. I believe that three salts may be formed containing respectively one, two, and three equivalents of sodium. One equivalent of the acid, I found, required for complete neutralisation, exactly three equivalents of pure, recently-ignited carbonate of soda. I could not obtain this salt in a fit state for analysis. I formed the salt with two equivalents of sodium by adding one equivalent of the acid to two other equivalents which had been previously neutralised, and evaporating the mixture on a water-bath till crystals were formed. These were pressed between folds of blotting-paper and recrystallised. Their composition is very probably represented by the formula:—

$$\left.\begin{array}{l} C_{12}H_5O_6{}''' \\ \quad Na_2 \\ \quad H \end{array}\right\} O_6 + 4HO.$$

Dried at 100° Cent., they gave 18·95 per cent. of sodium, instead of 18·7 per cent.

The salt containing one equivalent of sodium would not crystallise.

Tri-carballylate of Lime $\left.\begin{array}{l} C_{12}H_5O_6{}''' \\ Ca_3 \end{array}\right\} O_6 + 4HO.$—This salt is readily formed by adding a slight excess of hydrate of lime to a solution of tri-carballylic acid, and afterwards removing this excess by means of carbonic acid. On evaporating the filtered liquor, a white amorphous powder separates, which is the salt in question. It is very soluble in dilute acids, and sparingly soluble in water. It has the composition represented by the above formula. Dried at 100° Cent., it yielded 23·83 per cent. of calcium, instead of 23·30.

Tri-carballylate of Copper. $\left.\begin{array}{l} C_{12}H_5O_6{}''' \\ \quad Cu_3 \end{array}\right\} O_6.$—When sulphate of copper is added to a hot solution of tri-carballylate of soda, a beautiful bluish-green powder precipitates, which is the salt in question. It is insoluble in water, but soluble in dilute acids. Its composition accords with the formula I have given. I obtained from the salt dried at 100° Cent., 34·04 per cent. of metallic copper, instead of 35·45.

Tri-carballylate of Lead. $\left.\begin{array}{l} C_{12}H_5O_6{}''' \\ \quad Pb_3 \end{array}\right\} O_6.$—This salt is obtained by precipitating tri-carballylate of soda with an excess of acetate of lead. It is a perfectly white powder, insoluble in water, but soluble in dilute acids. The formula I have given correctly represents the composition. Dried at 100° Cent., it yielded 63·87 per cent. of metallic lead, instead of 64·23.

Tri-carballylate of Silver. $\left.\begin{array}{c} C_{12}H_5O_6''' \\ Ag_3 \end{array}\right\} O_6$. — When nitrate of silver is added to a solution of tri-carballylic acid, previously neutralised by ammonia, a white precipitate falls, which is the salt in question. This was very carefully washed with distilled water, dried in the water-oven, and analysed. The results I obtained, establish the above formula, as will be seen from the following table :—

		Theory.		Experiment.	
			per cent.	I.	II.
C_{12}	..	72	14·49	14·96	—
H_5	..	5	1·01	1·20	—
O_{12}	..	96	19·31	—	—
Ag_3	..	324	65·19		64·05
		497	100·00	—	

This salt is slightly soluble in water, and freely soluble in dilute nitric acid, and in ammonia.

That tri-carballylic acid is tribasic, is, I think, fully established by the manner in which it has been formed, and the composition of the salts and ethers I have just described.

Formulated according to the water and carbonic acid types, it is thus written :—

$$\left.\begin{array}{c} C_{12}H_5O_6''' \\ H_3 \end{array}\right\} O_6 ; \quad 3HO.C_6H_5'''\left\{\begin{array}{c} C_2O_2 \\ C_2O_2 \\ C_2O_2 \end{array}\right\} O_3$$

The manner of its formation inclines me to prefer the latter formula, although it is more cumbrous. Moreover, it brings out more clearly the relationship that exists between bi- and tribasic acids :—

$$2HO.C_4H_4''\left\{\begin{array}{c} C_2O_2 \\ C_2O_2 \end{array}\right\} O_2 ; \quad 3HO.C_6H_5'''\left\{\begin{array}{c} C_2O_2 \\ C_2O_2 \\ C_2O_2 \end{array}\right\} O_3$$

Succinic acid.
(bibasic).

Tri-carballylic acid.
(tribasic).

This acid is, I believe, at present the sole representative of its class. It will not, however, long remain so, as the process by which it has been obtained will, I have no doubt, prove to be of general application.

Tri-carballylic acid bears the same relation to citric acid that succinic bears to malic acid:

$C_{12}H_8O_{12}$ Tri-carballylic acid.	$C_8H_6O_8$ Succinic acid.
$C^1{}_2H_8O_{14}$ Citric acid.	$C_6H_8O_{10}$ Malic acid.

That this relationship exists not only on paper, but also in the nature of the bodies themselves, we can hardly doubt, when we call to mind that the acid in question has recently been generated from aconitic acid,* one of the products of the decomposition of citric acid by heat, and that acetone, another of these products, is closely allied to the radical from which tri-carballylic acid is derived.

Impressed with these considerations, I have endeavoured to transform this acid into citric acid. The resolution of this problem I have attempted in a great many ways, but hitherto without success. For instance, I have endeavoured to form the bromine compound of tri-carballylic acid, in the hope that it would yield the desired acid when subjected to the action of hydrated oxide of silver, according to the following equation:—

$$C_{12}H_7Br\,O_{12} + AgO.HO = C_{12}H_8O_{14} + AgBr.$$

My experiments in this direction were, however, cut short by my inability to form the brominated acid. I am at present engaged in endeavouring to solve the inverse problem, namely, the direct transformation of citric into tri-carballylic acid.

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* Ann. Ch. Pharm. cxxxii. 61.

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